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Review: Dye sensitized solar cells based on natural photosensitizers

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ABSTRACT

The performance of dye sensitized solar cells is mainly based on the dye as a sensitizer. Natural dyes have become a viable alternative to expensive and rare organic sensitizers because of its low cost, easy attainability, abundance in supply of raw materials and no environment threat. Various components of a plant such as the flower petals, leaves and bark have been tested as sensitizers. The nature of these pigments together with other parameters has resulted in varying performance. This review briefly discusses the emergence, operation and components of dye sensitized solar cells together with the work done on natural dye based dye sensitized solar cells over the years.

Contents

1. Dye sensitized solar cell background

Nanocrystalline cells surfaced in the late 19th century in conjunction with principles of photography. Dye sensitized solar cell (DSSC) was inspired by the energy and electron transfer mechanisms in natural photosynthesis and in dye sensitized silver halide emulsions used for photography. The first panchromatic film able to render the image of a scene realistically into black and white followed the work of Vofel after 1873, in which he associated dyes with the silver halide grains [1].

The use of dye-sensitization in photovoltaics remained rather unsuccessful until a breakthrough in 1991. In the Laboratory of Photonics and Interfaces in Ecole Polytechnique Federale de Lausanne, Switzerland, Grätzel and his co-workers developed a solar cell by the successful combination of nanostructured electrodes and efficient charge injection dyes. This cell was hence termed the dye sensitized nanostructured solar cell [2]. The use of sintered mesoporous titanium dioxide (TiO_2) was the breakthrough that established DSSC technology and raised the DSSC efficiency (η) from 1% (for cells having a non-porous TiO_2 surface) to 7%.

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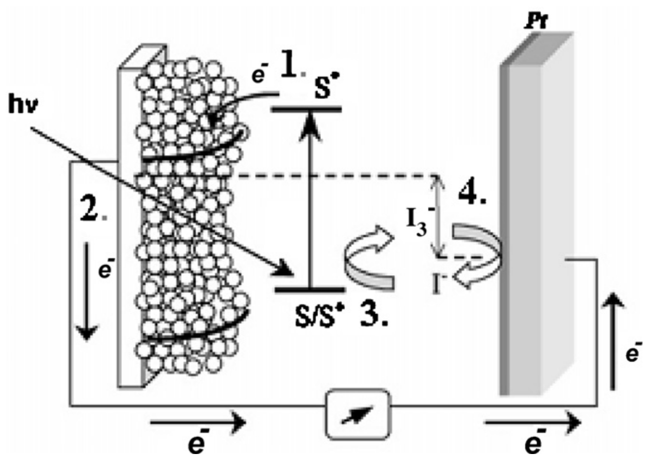


Fig. 1. Schematic structure of DSSC. 1. Upon light absorption, the dye (S) is promoted into an electronically excited state (S^*) from where it injects (within fs), an electron into the conduction band of a large bandgap semiconductor film (TiO_2), onto which it is adsorbed. 2. The electrons are transported through the TiO_2 film by diffusion before reaching the anode of the cell. 3. The positive charges resulting from the injection process are transferred into the liquid electrolyte by reaction of the dye cation (S^+) with the reduced species of a redox couple in the electrolyte solution. This leads to the generation of the charge neutral state of the sensitizer. 4. The most typical redox couple is I^-/I_3^-. After ionic diffusion, the carrier of the positive charge (I_3^-) reaches the cathode, where it releases its charge thus being reduced back to I^-.

DSSC photoelectrochemical cells have been subjected of a large number of experimental investigations since then. It falls in between solid-state photovoltaics and classical regenerative photoelectrochemical cell. The use of nanoscale constructs has given a major boost to the solar photon conversion. DSSC separates the optical absorption and charge separation process by associating a sensitizer with a wide-bandgap semiconductor of nanocrystalline morphology. Extended junction and nanostructured photoconversion device provide the pathway for light absorption and charge collection. Advantages of nanosized semiconductor structures and particles include increased carrier lifetimes arising from space quantization, enhanced redox potentials of photogenerated holes and electron arising from increased effective bandgap. It is now possible to completely depart from the classical solid state junction device by replacing the phase contacting the semiconductor by an electrolyte, thereby forming a DSSC [3].

According to [4] conversion efficiency records of 8.12%, 10.10%, 10.40% and 9.90% were announced at Energy Research Centre of The Netherlands, École Polytechnique Fédérale de Lausanne, Sharp Corporation and Arakawa group, respectively for strip solar cells with aperture area of 1–5 cm^2. Apparently, the use of high haze TiO_2 electrodes led to the highest efficiency till date, standing at 11.10% [5]. Efforts are continually being undertaken to improve the performance of DSSC and hence the competitiveness of this technology in the world market.

2. DSSC operation

DSSC parallels photosynthesis in the use of a dye as the light harvester to produce excited electrons, TiO_2 replacing carbon dioxide as the electron acceptor, iodide/triiodide (I^-/I_3^-) replacing water and oxygen as the electron donor and oxidation product and a multilayer structure (similar to the thylakoid membrane) to enhance both the light absorption and electron collection efficiency.

The light-driven electrochemical process in DSSC is regenerative as shown in Fig. 1 and the working voltage produced by the device is the difference between the chemical potential of the TiO_2 (Fermi level) and the redox potential of the mediator I^-/I_3^- [6]. Like photosynthesis, DSSC is a molecular machine that is one of the first devices to go beyond microelectronics into the realm of nanotechnology [7].

The latter process typically requires a catalytic amount of counter electrode, typically platinum (Pt) on the cathode surface. The process control is governed by kinetic competition. In optimized systems, a favorable kinetic balance assures that loss mechanisms such as the thermalization of the dye excited state and other recombination processes are largely suppressed [8].

The operating cycle can be summarized in chemical reaction terminology as [9]:

Anode:

$$S + h\nu \rightarrow S* \quad \text{Absorption} \tag{1}$$

$$S* \rightarrow S^+ + (TiO_2) \quad \text{Electron injection} \tag{2}$$

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \quad \text{Regeneration} \tag{3}$$

Cathode:

$$I_3^- + 2e^-(Pt) \rightarrow 3I^- \tag{4}$$

Cell:

$$e^-(Pt) + h\nu \rightarrow 3I^- \tag{5}$$

The operation of the cell is regenerative in nature since no chemical substances are neither consumed nor produced during the working cycle, as visualized in the cell reaction (5).

3. DSSC components

DSSC converts visible light into electricity based on the sensitization of wide bandgap semiconductors and is primarily comprised of photoelectrode, redox electrolyte and counter electrode. Other materials include transparent conducting oxide and sealing agents. DSSC components have gone under various developments over the years in order to enhance the efficiency of the cell.

3.1. Photosensitizers

An efficient photosensitizer must fulfill certain requirements such as [7]:

- An intense absorption in the visible region.
- Strong adsorption onto the semiconductor surface.
- Efficient electron injection into the conduction band of the semiconductor.
- It should possess several =O or –OH groups capable of chelating to the Ti(IV) sites on the TiO_2 surface.

Likewise, it must be rapidly regenerated by the mediator layer to avoid electron recombination processes and be fairly stable, both in the ground and excited states. The ideal sensitizer for a photovoltaic cell converting standard air mass (AM) 1.5 sunlight to electricity, must absorb all light below a threshold wavelength of about 900 nm, which is equivalent to a semiconductor with a bandgap of 1.4 eV [10].

Overall the cell performance is subjected to a number of factors but fundamental considerations relating to the dye are how efficiently:

- The molecules absorb incident photons.
- Photons are converted to electron–hole pairs.
- Separation and collection occurs.

The finest photovoltaic performance in terms of both conversion yield and long term stability, has so far been achieved with

polypyridyl complexes of Ruthenium (Ru) developed by the Grätzel group: N3, N719 and 'black' dyes. Further to superior light harvesting properties and durability, a significant advantage of these dyes lie in the metal–ligand charge transfer transition through which the photoelectric charge is injected into TiO_2. In Ru complexes, this transfer takes place at a much faster rate than the back reaction, in which the electron recombines with the oxidized dye molecule rather than flowing through the circuit and performing work [11].

However, the use of these expensive Ru metals, derived from relatively scarce natural resources corresponds to a relatively heavy environmental burden [12]. Hence, it is possible to use natural dyes as alternative photosensitizers with appreciable efficiencies. Their advantages over synthetic dyes include easy availability, abundance in supply, can be applied without further purification, environmentally friendly and they considerably reduce the cost of devices [13]. Natural dye based DSSCs have been fully discussed in Section 4.

3.2. Semiconductor film electrode

The semiconductor structure, typically 10 μm thick with a porosity of 50%, has a surface area available for dye chemisorption over a thousand times than that of a flat, unstructured electrode of the same size. If the dye is chemisorbed as a monomolecular layer, enough can be retained on a given area of electrode to provide absorption of essentially all the incident light. The need for DSSC to absorb far more of the incident light was the driving force for the development of mesoscopic semiconductor material (minutely structured materials with an enormous internal surface area).

Mesoporous oxide films are made up of arrays of tiny crystals measuring a few nanometers across. Oxides such as TiO_2, zinc oxide, tin oxide, niobium oxide or chalcogenides such as cadmium selenide are the preferred photoelectrodes. These are connected to allow electronic conduction to take place. Between the particles are mesoscopic pores filled with a semiconducting or a conducting medium such as a p-type semiconductor, a polymer, a hole transmitter and an electrolyte. The net result is a junction of extremely large contact area between two interpenetrating, individually continuous networks [14].

Photoelectrodes made of materials such as silicon and cadmium sulfide decompose under irradiance in solution owing to photocorrosion. In contrast, oxide semiconductor materials, especially TiO_2, have good chemical stability under visible irradiation in solution [15]. It has been found that TiO_2 is a stable photoelectrode in photoelectrochemical systems even under extreme operating conditions. It is cheap, readily available and non-toxic and is normally used as dye in white paint and toothpastes. Its conduction band edge coincides well with the excited electronic level of anthocyanin containing dyes which is an important condition to be satisfied for the injection of electrons from the dye molecule to the semiconductor [16].

The high dielectric constant of TiO_2 ($\epsilon = 80$ for anatase) provides good electrostatic shielding of the injected electron from the oxidized dye molecule attached to the TiO_2, thus preventing their recombination before reduction of the dye by the redox electrolyte. High refractive index of TiO_2 ($n = 2.5$ for anatase) results in efficient diffuse scattering of the light inside the porous photoelectrode, which significantly enhances the light absorption [17].

According to [18], dye adsorption and microstructure of the TiO_2 film are important properties when it is used as photoelectrode for DSSCs. TiO_2 occurs in three crystalline forms – rutile, anatase and brookite. Anatase appears as pyramid-like crystals and is stable at low temperatures whereas needle-like rutile crystals are dominantly formed in high temperature processes. Rutile absorbs 4% of the incident light in the near-UV region, and band gap excitation generated holes that act as strong oxidants reducing the long-term stability of the DSSCs. Brookite is difficult to produce and is therefore not considered in DSSC application. The band-gap of anatase is 3.2 eV at an absorption edge of 388 nm and that of rutile is 3.0 eV at an absorption edge of 413 nm [19]. The common techniques employed in the preparation of TiO_2 films include the doctor blade technique, screen printing, electrophoretic deposition and tape casting method.

3.3. Electrolyte

Short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) considerably depend on the electrolyte. The electrolyte used in DSSC mostly contains I^-/I_3^- redox ions, which mediate electrons between the TiO_2 photoelectrode and the counter electrode. The first DSSC used organic liquid electrolyte containing lithium iodide/iodine. Organic solvent is a basic component of the liquid electrolytes as it provides an environment for I^-/I_3^- dissolution and diffusion. Physical parameters such as donor number, dielectric constant and viscosity affect the efficiency of the cell [20].

The electrolyte is a neutral sink of I^- and I_3^- feeding the reactions (3) and (4) at the electrodes and maintaining the redox potential in the bulk of the electrolyte via the fast redox reaction of the I^-/I_3^- pair. This redox reaction in the electrolyte is a two-electron reaction [21]:

$$3I^- \rightarrow I_3^- + 2e^- \tag{6}$$

which is composed of a series of successive reactions:

$$(I^- \rightarrow I + e^-) \times 2 \quad \text{charge transfer reaction} \tag{7}$$

$$2I \rightarrow I_2 \quad \text{fast chemical reaction} \tag{8}$$

$$I_2 + I^- \rightarrow I_3^- \quad \text{fast chemical reaction} \tag{9}$$

Bromine (Br^-/Br_2) and hydroquinone have also been used as redox electrolyte for DSSC, but the iodine redox electrolyte gives the best performance [15]. At the TiO_2 electrode, the oxidized dye left behind by the electron injected to the TiO_2, is regenerated by I^- in the electrolyte in the reaction (3) while at the counter electrode, I_3^- is reduced to I^- in the reaction (4). In other words, I_3^- is produced at the TiO_2 electrode and consumed at the counter electrode and thus diffused across the electrolyte correspondingly. This is why I_3^- is often labeled as the hole carrier which draws similarities with the conventional p–n junction solar cells. Similarly, I^- is produced at the counter electrode and diffused to the opposite direction in the electrolyte.

Room temperature ionic liquid has good chemical and thermal stability, negligible vapor pressure, non flammability and high ionic conductivity. When incorporated into DSSCs, they serve both as a source of iodide and the solvent itself. Liquid electrolyte based organic solvent usually have high ionic conductivity and excellent interfacial contact property however there still exist problems such as leakage and volatility of the solvent which affect the long term performance of DSSCs [20].

A disadvantage of liquid electrolyte is that it may limit device stability because the liquid may evaporate when the cell is imperfectly sealed. Penetration of water or oxygen molecules and their reaction with the electrolyte may also worsen cell performance. Liquid electrolytes also make the construction of multi-cell modules difficult because cells must be connected electrically yet separated chemically, preferably on a single substrate. Among all of the solid-state cells, the one containing a p-type semiconductor possessed the advantage of easy preparation and higher stability while the cells employing polymer electrolytes showed higher efficiency and wider practical future use with the proper encapsulation [22].

Table 1
Pigments in plants.

Pigment	Common type	Occurrence
Betalains	Betacyanins Betaxanthins	Caryophyllales and some fungi
Carotenoids	Carotenes	Photosynthetic plants and bacteria
	Xanthophylls	Retained from the diet by some birds, fish and crustaceans
Chlorophyll	Chlorophyll	All photosynthetic plants
Flavonoids	Anthocyanins Aurones Chalcones Flavonols Proanthocyanidins	Widespread and common in plants including angiosperms, gymnosperms, ferns and bryophytes

3.4. Counter electrode

The prerequisite of a material used as counter electrode in DSSC is that it should have a low charge transfer resistance and high exchange current densities for the reduction of the oxidized form of the charge mediator [23]. The counter electrode serves to transfer electrons arriving from the external circuit back to the redox electrolyte. It also has to carry the photocurrent over the width of each solar cell. Hence, it must be well conducting and exhibit a low overvoltage for reduction of the redox couple. Till now, Pt has been the desired material for the counter electrode since it is an excellent catalyst for I_3^- reduction [15].

An interesting low cost alternative for Pt is carbon (C), because it combines sufficient conductivity and heat resistance as well as corrosion resistance and electrocatalytic activity for the I_3^- reduction [17]. Porous C electrodes are easily prepared from graphite powder, which consists of plate like crystals that, on deposition from a liquid dispersion and drying, will preferentially align in the plane of the counter electrodes, resulting in a high conductivity in this plane. Pt/C black counter electrode for DSSC and achieved 6.72% efficiency under one sun illumination. Pt/C black electrode showed the same efficiency and lower cost compared with Pt electrode alone [24].

4. Natural dyes

Natural dyes provide a viable alternative to expensive organic based DSSCs. Various components of a plant has been tested over the last two decades as suitable sensitizers.

4.1. Plant pigmentation

Plant pigmentation occurs due to the electronic structure of the pigment interacting with sunlight to alter the wavelengths that are either transmitted or reflected by the plant tissue. The specific color will depend on the abilities of the observer. Humans without color blindness can detect wavelengths between approximately 430 and 680 nm, representing the visible spectrum. The pigments can be described in two ways: the wavelength of maximum absorbance (λ_{max}) and the color perceived by humans. Table 1 illustrates the grouping of plant pigments based on the common structure and biosynthetic basis [25].

4.1.1. Carotenoids

Carotenoid pigments provide many fruits and flowers with distinctive red, orange and yellow colors and a number of carotenoid-derived aromas. The range of colors is expanded by diverse modifications to the simple polyene chain structure. The carotenoid backbone is either linear or contains cyclic end groups and the two major classes constitute of carotenes and their oxygenated derivates, the xanthophylls. Carotenoids are involved in photosystem assembly and contribute to light harvesting by absorbing light energy in a region of the visible spectrum where chlorophyll absorption is lower and by transferring the absorbed energy to chlorophyll. It also provides protection from excess light via energy dissipation, free radical detoxification and limits damage to membranes [25].

4.1.2. Flavonoid

Flavonoids and their conjugates form a very large group of natural products. They are found in many plant tissues, where they are inside the cells or on the surfaces of different plant organs. The term "flavonoid" is generally used to describe a broad collection of natural products that include a C_6–C_3–C_6 carbon framework or more specially phenylbenzopyran functionality. Depending on the position of the linkage of the aromatic ring to the benzopyrano (chromano) moiety, this group of natural products may be divided into three classes: the flavonoids (2-phenylbenzopyrans), isoflavonoids (3-benzopyrans) and the neoflavonoids (4-bezopyrans). These groups usually share a common chalcone precursor and therefore are biogenetically and structurally related. Natural products such as chalcones and aurones also contain a C_6–C_3–C_6 backbone and are considered as minor flavonoids [26].

Flavonoids have a 15-carbon (C_{15}) base structure comprised of two phenyl rings connected by a three-carbon bridge that usually forms a third ring. The various colors of flavonoids are determined by the degree of oxidation of the C-ring. Despite the similarities in structure, only some flavonoids have the ability to absorb light in the visible region of the spectrum and are thus pigments. Pigment molecules are characterized by having unbound or loosely bound electrons. For such molecules, the energy required for excitation of the electrons to a higher energy level is lowered, allowing the molecule to be energized by light within the visible range. The color of the pigment is determined by the particular wavelengths of visible light that are absorbed by the molecule and those by the particular wavelengths of visible light that are absorbed by the molecule and those that are reflected or scattered. The structural features of a flavonoid pigment are the degrees of double bond conjugation and oxygenation (in the form of hydroxylation).

For many angiosperms, color is the key to attracting pollinators, whether they are bees, butterflies, other insects or birds, although it is frequently one of a number of factors including fragrance, floral shape and nectar reward. In plants, flavonoids have several functions including attracting insects for pollination and dispersal of seeds, acting in defense systems such as UV-B protectants and phytoalexins, signaling between plants and microbes and regulating auxin transport. Flavonoids may form UV–visible patterning in petals, often in combination with UV-reflective carotenoid pigments. While in most flowers, color begins with the production and accumulation of flavonoid chromophores, other factors both intrinsic and extrinsic, come into play that determine the actual color that is manifested by the flower. Flavonoid pigmentation is basically based on three components: the primary structures of the flavonoids, secondary structures of these molecules due to pH and tertiary structures arising from self-association and inter and intramolecular interactions [25].

Anthocyanins, proanthocyanidins (condensed tannins) and flavonols are three major subclasses of flavonoid compounds. Anthocyanins do not show their brilliant colors until they are accumulated in the acidic vacuoles. Some flavonols have a protective role as UV-B filters and they also could function as copigments for anthocyanins for special tissues [26].

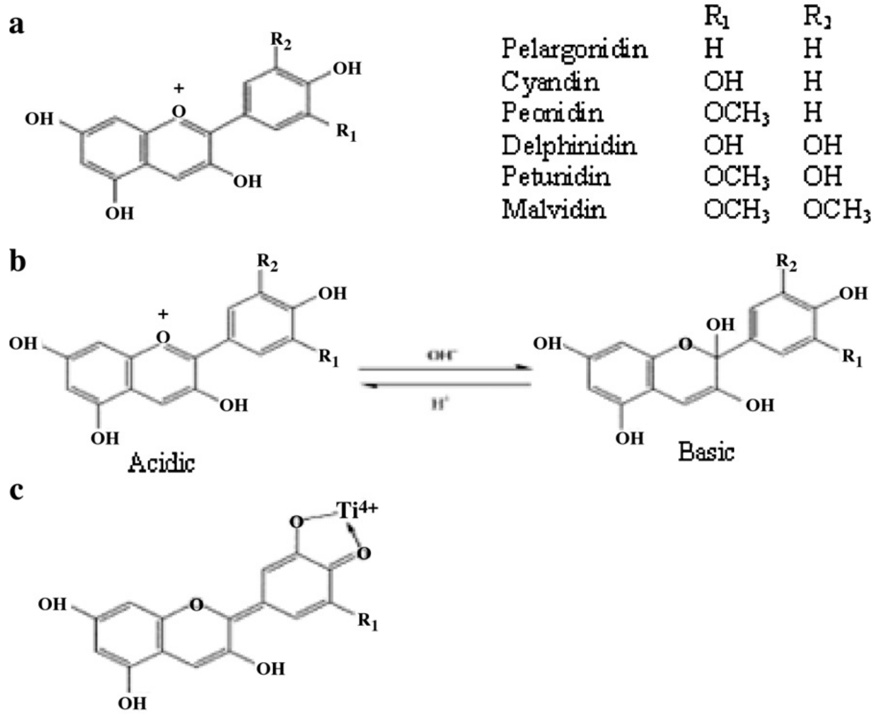


Fig. 2. (a) Basic chemical structures of the most abundant anthocyanidins. (b) Chemical structures of anthocyanidins in acidic and basic media. (c) Chelation mechanism of anthocyanidins with TiO_2.

4.1.3. Anthocyanins

The anthocyanins constitute a major flavonoid group that is responsible for cyanic colors ranging from salmon pink through red and violet to dark blue of most flowers, fruits and leaves of angiosperms. Sometimes they are present in other plant tissues such as roots, tubers and stems [27]. The most common anthocyanidins found in flowers are pelagonidin (orange), cyanidin (orange-red), delpinidin (blue-red), petunidin (blue-red) and malvidin (blue-red) [28]. Anthocyanins from various plants give different sensitizing performances [13]. They are the most abundant and widespread of the flavonoid pigments that absorb light at the longest wavelength.

Anthocyanins are usually in solution within the vacuole, although they may sometimes be located in spherical vesicles called 'anthocyanoplasts', in which structural modifications of the C_{15} nucleus occurs [29]. They are a group of naturally occurring phenolic compounds responsible for the color of many flowers, fruits (particularly in berries) and vegetables. They are glycosylated polyhyroxy or polymethoxy derivatives of 2-phenylbenzopyrylium or flavylium salts, which consist of three six-membered rings as illustrated in Fig. 2.

5. Photoelectrochemical parameters

Table 2 summarizes the photoelectrochemical parameters of DSSCs using a range of natural dyes as photosensitizers subject to the work done by various pioneers. It demonstrates typical characteristics such as η, J_{sc}, V_{oc} and fill factor (FF) values.

The FF is a measure of the junction quality and series resistance of the DSSC and is typically calculated as:

$$FF = \frac{J_m \times V_m}{J_{sc} \times V_{oc}} \quad (10)$$

where J_m and V_m are the maximum current and voltage, respectively.

Solar energy-to-electricity conversion efficiency, η, under sunlight irradiation (e.g., AM 1.5) can be obtained by Eq. (11):

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (11)$$

where P_{in} is the power of incident light and measured in mW cm^{-2} using a solarimeter and J_{sc} is measured in mA cm^{-2} [30].

6. Preparation of dye solutions and electrodes

According to Table 2, the best performance has been produced by Red turnip based on the work performed by [38]. This work resulted in a remarkable J_{sc} of 9.5 mA cm^{-2} and a high incident photon to current conversion efficiency of 65% at 470 nm. Red turnip originally grew wild in the Mediterranean area, particularly in regions that have cold nights during the spring season. Its ball-shaped red roots contain a high concentration of betalain pigments. The red turnip extract was obtained by immersing its slices in 0.1 M HCl solution, overnight. If properly stored, protected from direct sunlight and refrigerated at about +4 °C, the acidic natural dye solutions are usually stable, with a deactivation half-time of more than 12 months. Sol–gel procedure was used for preparing titanium oxide nanoparticles.

The fourth highest efficiency also followed the work of [38]. The same procedure was used for preparation of the dye. The efficiency of Wild Sicilian prickly pear based DSSC was found to be 1.19%. The pigment present in Wild Sicilian prickly pear and red turnip is shown in Fig. 3.

Work done by [37] produced the second best efficiency. DSSC sensitized with pomegranate juice produced an efficiency of 1.50%. TiO_2 was deposited by tape casting technique. Pomegranate juice mainly contains cyanin derivatives and exists as flavylium at natural pH. Flavylium is red in color and strongly bond with Ti^{4+} via emanating H_2O molecule.

The third best performance has been delivered by shiso leaf pigments. The shiso plant is well known in Japan as a vegetable

Table 2
Photoelectrochemical parameters of natural dye based DSSCs.

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)	Reference
Rosella	1.63	0.40	0.57	0.37	[13]
Blue pea	0.37	0.37	0.33	0.05	
Mixed rosella-blue pea	0.82	0.38	0.47	0.15	
Black rice	1.14	0.55	0.52	–	[31]
Capsicum	0.23	0.41	0.63	–	
Rosa xanthina	0.64	0.49	0.52	–	
Kelp	0.43	0.44	0.62	–	
Erythrina variegate	0.78	0.48	0.55	–	
Bixin	1.10	0.57	0.59	0.37	[32]
Annatto	0.53	0.56	0.66	0.19	
Norbixin	0.38	0.53	0.64	0.13	
Crocetin	2.84	0.43	0.46	0.56	[33]
Crocin	0.45	0.58	0.60	0.16	
Fruit of Calafate	6.20	0.47	0.36	–	[34]
Syrup of Calafate	1.50	0.38	0.20	–	
Skin of Jaboticaba	7.20	0.59	0.54	–	
Red Sicilian orange	3.84	0.34	0.50	–	[35]
Purple eggplant extract	3.40	0.35	0.40	–	
Dragon fruit	0.20	0.22	0.30	0.22	[36]
Pomegranate juice	0.20	0.40	0.45	1.50	[37]
Red turnip	9.50	0.43	0.37	1.70	[38]
Wild Sicilian prickly pear	8.20	0.38	0.38	1.19	
Sicilian Indian fig	2.70	0.38	0.54	0.50	
Bougainvillea	2.10	0.30	0.57	0.36	
Shisonin	3.56	0.55	0.51	1.01	[39]
Shisonin and chlorophyll	4.80	0.53	0.51	1.31	
Chlorophyll	3.52	0.43	0.39	0.59	
Hibiscus surattensis	5.45	0.39	0.54	1.14	[28]
Sesbania grandiflora	4.40	0.41	0.57	1.02	
Hibiscus rosasinesis	4.04	0.40	0.63	1.02	
Nerium olender	2.46	0.41	0.59	0.59	
Ixora macrothyrsa	1.31	0.40	0.57	0.30	
Rhododendron arboretum zeylanium	1.15	0.40	0.64	0.29	
Begonia	0.63	0.54	0.72	0.24	[40]
Tangerine peel	0.74	0.59	0.63	0.28	
Rhododendron	1.61	0.59	0.61	0.57	
Fructus lyciia	0.53	0.69	0.47	0.17	
Marigold	0.51	0.54	0.83	0.23	
Perilla	1.36	0.52	0.70	0.50	
Herba artemisiae scopariae	1.03	0.48	0.68	0.34	
China loropetal	0.84	0.52	0.63	0.27	
Yellow rose	0.74	0.61	0.57	0.26	
Flowery knotweed	0.60	0.55	0.63	0.21	
Bauhinia tree	0.96	0.57	0.66	0.36	
Petunia	0.85	0.62	0.61	0.32	
Lithospermum	0.14	0.34	0.59	0.03	
Violet	1.02	0.50	0.65	0.33	
Chinese rose	0.90	0.48	0.62	0.27	
Mangosteen pericarp	2.69	0.67	0.63	1.17	
Rose	0.97	0.60	0.66	0.38	
Lily	0.51	0.50	0.67	0.17	
Coffee	0.85	0.56	0.69	0.33	
Broadleaf holly leafbase	1.19	0.61	0.65	0.47	
Red *Bougainvillea glabra*	2.34	0.26	0.74	0.45	[41]
Violet *Bougainvillea glabra*	1.86	0.23	0.71	0.31	
Red *Bougainvillea spectabilis*	2.29	0.28	0.76	0.48	
Violet *Bougainvillea spectabilis*	1.88	0.25	0.73	0.35	
Spinach	0.47	0.55	0.51	0.13	[42]
Ipomoea	0.91	0.54	0.56	0.28	
Bongainvillea brasiliensis	5.00	0.25	0.36	0.45	[43] (water based DSSC)
Garcinia suubelliptica	6.48	0.32	0.33	0.69	
Ficus reusa	7.85	0.52	0.29	1.18	
Rhoeo spathacea	10.9	0.50	0.27	1.49	

and the leaf extract and is used as a food colorant. Leaves of this plant contain two anthocyanin pigments referred to as shisonin and malonylshisonin (Fig. 4) as well as chlorophyll and other photosynthetic pigments.

Shiso leaves were lightly crushed and boiled in water–acetone mixture containing acetic acid. An efficiency as high as 1.30%, J_{sc} of 4.80 mA cm^{-2} and V_{oc} of 0.53 V. Shisonin also produced a promising performance of 1.01% [39].

Natural dyes were extracted from natural materials such as flowers, leaves, fruits, traditional Chinese medicines and beverages and used as sensitizers to fabricate DSSCs. The photoelectrochemical performance of the DSSCs based on these dyes showed that V_{oc} varied from 0.38 to 0.69 V and J_{sc} ranged from 0.14 to 2.69 mA cm^{-2}. Specifically, a high V_{oc} of 0.69 V was obtained from the dye extracted from mangosteen pericarp sensitizer. The photoelectric conversion efficiency of the DSSC sensitized by the ethanol extract

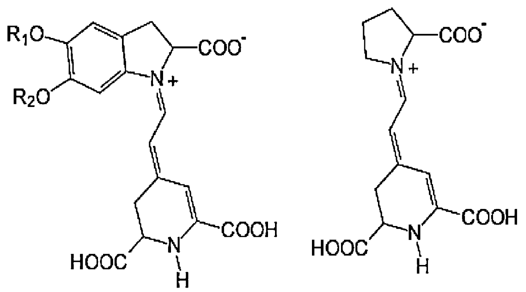
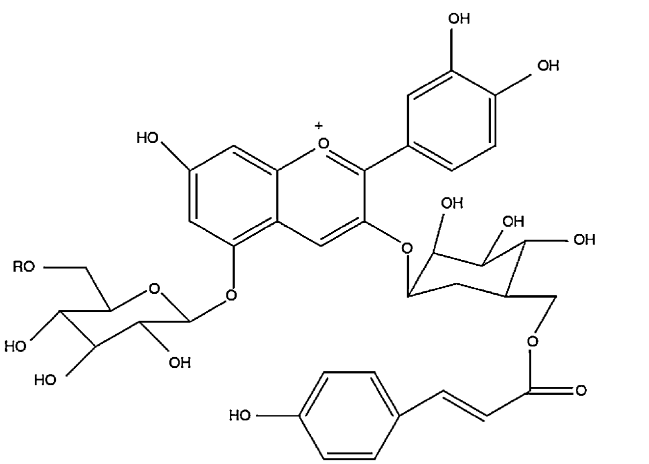


Fig. 3. General structures of the main betalain dyes contained in the studied extracts: (1) betacyanin and (2) indicaxanthin R_1 and R_2 = H (betanidin) or R_1 = β-D-glucose and R_2 = H (betanin).



Shisonin: R = H Malonylshisonin: R = Malonic acid

Fig. 4. Molecular structure of shisonin.

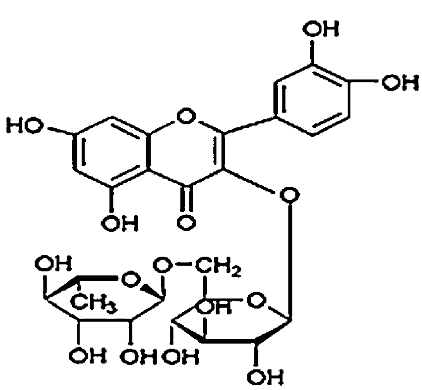


Fig. 5. Basic molecular structures for the main components of the extracts of mangosteen pericarp with ethyl acetate.

of mangosteen pericarp (Fig. 5) without purification reached 1.17% which is the fifth best performance among natural dyes. The TiO_2 films were prepared by doctor blade technique [40].

Various natural pigments containing anthocyanins were extracted from tropical flowers. J_{sc} ranging from 1.1 to 5.4 mA cm^{-2} and V_{oc} ranging from 0.39 to 0.41 V were obtained. The overall efficiency and FF of these cells varied from 0.20% to 1.14% and 0.53 to 0.64, respectively. The extract from *Hibiscus surattensis* gave the best photosensitized effect of 1.14%. TiO_2 films were prepared by the doctor blade method and the pigments were extracted in ethanol. The content of delphinidin-derived anthocyanins and flavonol-glycosides was high in the magenta-colored *H. surattensis*. *Sesbania grandiflora* and *Hibiscus rosasinesis* also produced promising efficiency of 1.02%. A variable amount of flavonolglycosides was obtained from the two extracts [28].

The DSSCs contained different pigments which produced diverse photosensitizing effect, justifying that only selected pigments are capable of converting sunlight into electricity. The best performance was noted for betalain pigment. Hence it can be concluded that the interaction between betalain and TiO_2 is high. Cyanin, shisonin and malonylshisonin also formed better bonds with TiO_2 compared to other plant pigments. Furthermore, the cost performance [conversion efficiency]/[cost of dye] of natural dye based DSSCs is quite high when compared to organic based DSSCs.

Gold nanoparticles were fabricated as a Schottky barrier on a TiO_2 electrode, which adsorbed the free natural dyes in the water-based dye-sensitized solar cell with the aqueous electrolyte of $Ce^{4+/3+}$ system. Promising efficiencies were obtained from using natural dyes in water based DSSCs. The extract of the natural dye *Rhoeo spathacea* Stearn reached the solar conversion efficiency of 1.49%, which had the best photosensitized effect of the water-based DSSC [43].

7. Why is the performance of natural dye based DSSC low?

Rest of the natural dye based DSSC produced efficiencies less than 1%, ranging from 0.05% to 0.59% as illustrated in Table 2. The reason for such low efficiency is that the interaction between betalain and TiO_2 would have been low. The structure of the pigment also affects the performance, i.e., if the structure has a longer R group, this result in the steric hindrance for the pigment to form bond with the oxide surface of the TiO_2 and hence prevents the molecule from arraying on the TiO_2 film effectively. Hence there is lack of electron transfer from the dye molecules to the conduction band of TiO_2. The intensity and range of light absorption of the extract also affects the performance. The distance between the dye skeleton and the point connected to the TiO_2 surface facilitates electron transfer from the dye molecule to the TiO_2 surface which accounts for the performance of the cell [13].

The interaction between TiO_2 and the dye plays an important role towards the efficiency of DSSCs. In general, natural dyes suffer from low V_{oc}. According to [38], this can be due to possible inefficient electron/dye cation recombination pathways and the acidic dye adsorption environment. In fact H^+ are the potential determining ions for TiO_2 and that proton adsorption causes a positive shift of the Fermi level of the TiO_2, thus limiting the maximum photovoltage that could be delivered by the cells.

According to [40], the charge transfer in the TiO_2/dye/electrolyte interface resistance leads to a decrease in J_{sc}. Thus, introducing a functional group, such as carboxyl group and optimizing the structure of the natural dye are necessary to improve the efficiency of natural dye based DSSCs.

Some complication such as dye aggregation on nanocrystalline film produces absorptivity that results in no electron injection. Dye aggregation is a serious issue that occurs when compounds fill the free space between the dye molecules, partially blocking the physical contact between the iodine solution and TiO_2 semiconductor film surface, reducing reaction and inhibiting dye aggregation [35].

8. Recommendations

Many factors affect the performance of DSSC. Some parameters include the nature of the pigment, light spectrum and intensity, the thickness of the TiO_2 layer, the size of the active area, the nature of the electrolyte salt and the extracting solvent. For an efficient solar cell, rapid charge injection and transport and intense visible light absorption are necessary. Although the efficiencies obtained with these natural dyes are still below the present conditions for

large scale practical application, the results are encouraging and may boost additional studies oriented to the search of new natural sensitizers and optimization of the solar cell [38].

According to [6] characterization of the loss of carriers due to electron recapture by the electrolyte as the electrons drift through the film to the back contact is important for future research. Also finding various additives to improve V_{oc} can result in an increase in energy conversion. The dye can be affected by oxygen, pH, temperature and other variables that lead to its degradation and affect the performance of DSSCs [34]. Hence further investigations can be performed on this subject.

Solid state electrolytes are possible replacements to the liquid ones, however the efficiency becomes low. Hence a possible future research could be to find ways of improving its performance. Stability of natural dye based DSSC is also a major concern for the natural dye based DSSC. The implication of decrease in stability makes the entry of this device into practical applications, difficult. Therefore further studies must be performed to improve the stability of the cell.

9. Conclusions

Overall, natural dyes as sensitizers for DSSCs are promising alternative to organic dyes. They offer environmental friendliness, low-cost production, designable polychrome modules, simple preparation technique and wide availability. Although the efficiencies obtained with the natural dyes are below the requirements for large scale production, the results are hopeful and can boost additional studies oriented to the search of new natural sensitizers and to the optimization of solar cell components compatible with such dyes. The highest efficiency of 1.70% has been reached by Red Turnip which contains betalain pigment. However, there still remains room for further development for the commercialization of this technology.

References

[1] West W.Proceedings of Vogel Centennial Symposium. Photographic Science and Engineering 1974;18:35.
[2] O'Regan B, Grätzel M. A low-cost, high-efficiency solar-cell based on dye sensitized colloidal TiO_2 films. Nature 1991;353:737–40.
[3] Archer MD, Nozik AJ. Nanostructured and photoelectrochemical systems for solar photon conversion. London, UK: Imperial College Press; 2008.
[4] Kong F, Dai S, Wang K. Review article: review of recent progress in dye-sensitized solar cells. Advances in OptoElectronics 2007;2007: 1–13.
[5] Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han L. Dye-sensitized solar cells with conversion efficiency of 11.1%. Japanese Journal of Applied Physics 2006;45:L638–40.
[6] Cherepy NJ, Smestad GP, Grätzel M, Zhang JZ. Ultrafast electron injection: implications for a photoelectrochemical cell utilizing an anthocyanin dye-sensitized TiO_2 nanocrystalline electrode. Journal of Physical Chemistry 1997;101:9342–51.
[7] Smestad GP. Education and solar conversion: demonstrating electron transfer. Solar Energy Materials and Solar Cells 1998;55:157–78.
[8] Lenzmann FO, Kroon JM. Review: recent advances in dye-sensitized solar cells. Advances in OptoElectronics 2007;2007:1–27.
[9] Matthews D, Infelta P, Grätzel M. Calculation of the photocurrent-potential characteristic for regenerative, sensitized semiconductor electrodes. Solar Energy Materials and Solar Cells 1996;44:119–55.
[10] Wan H. Dye sensitized solar cells, literature seminar. AL, United States of America: The University of Alabama; 2004.
[11] Ryan M. Progress in ruthenium complexes for dye sensitised solar cells. Platinum Metals Review 2009;53:216–8.
[12] Reijnders L. Design issues for improved environmental performance of dye-sensitized and organic nanoparticulate solar cells. Journal of Cleaner Production 2010;18:4307–12.
[13] Wongcharee K, Meeyoo V, Chavadej S. Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers. Solar Energy Materials and Solar Cells 2007;91:566–71.
[14] Grätzel M. Photoelectrochemical cells. Nature 2001;414:338–44.
[15] Luque A, Hegedus S. Handbook of photovoltaic science and engineering. The Netherlands: Elsevier; 2003.
[16] Olea A, Ponce G, Sebastian PJ. Electron transfer via organic dyes for solar conversion. Solar Energy Materials and Solar Cells 1999;59:137–43.
[17] Kay A, Grätzel M. Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. Solar Energy Materials and Solar Cells 1996;44:99–117.
[18] Tang X, Qian J, Wang Z, Wang H, Feng Q, Liu G. Comparison of low crystallinity TiO_2 film with nanocrystalline anatase film for dye-sensitized solar cells. Journal of Colloidal and Interface Science 2009;330:386–91.
[19] Kalyanasundaram K, Grätzel M. Applications of functionalized transition metal complexes in photonic and optoelectronic devices. Coordination Chemistry Reviews 1998;177:347–414.
[20] Wu, Lan JZ, Hao S, Li P, Lin J, Huang M, et al. Progress on the electrolytes for dye-sensitized solar cells. Pure and Applied Chemistry 2008;80:2241–58.
[21] Ferber J, Stangl R, Luther J. An electrical model of the dye-sensitized solar cell. Solar Energy Materials and Solar Cells 1998;53:29–54.
[22] Lin CK, Yang TJ, Feng YC, Tsung TT, Su CY. Characterization of electrophoretically deposited nanocrystalline titanium dioxide films. Surface and Coating Technology 2006;200:3184–9.
[23] Anandan S. Recent improvements and arising challenges in dye-sensitized solar cells. Solar Energy Materials and Solar Cells 2007;91:843–6.
[24] Li P, Wu J, Lin J, Huang M, Huang Y, Li Q. High performance and low platinum loading Pt/carbon black counter electrode for dye-sensitized solar cells. Solar Energy 2009;83:845–9.
[25] Davies K. Plant pigments and their manipulation. USA: Blackwell Publishing Ltd.; 2004.
[26] Grotewold E. The science of flavonoids. Columbus, USA: Springer; 2006.
[27] Andersen ØM, Markham KR. Flavonoids chemistry, biochemistry and applica-tion. NY, USA: CRC Press Taylor & Francis Group; 2006.
[28] Fernando JMRV, Senadeera GKR. Natural anthocyanins as photosensitizers for dye-sensitized solar devices. Current Science 2008;95:663–6.
[29] Harborne JB. The flavonoids advances in research since 1986. London, England: Chapman & Hall; 1994.
[30] Wenham SR, Green MA, Watt ME, Corkish R. Applied photovoltaics. Australia: Centre for Photovoltaic Engineering; 2006.
[31] Hao S, Wu J, Huang Y, Lin J. Natural dyes as photosensitizers for dye-sensitized solar cell. Solar Energy 2006;80:209–14.
[32] Gòmez-Ortíz NM, Vázquez-Maldonado IA, Pérez-Espadas AR, Mena-Rejón GJ, Azamar-Barrios JA, Oskam G. Dye-sensitized solar cells with natural dyes extracted from achiote seeds. Solar Energy Materials and Solar Cells 2009;94:40–4.
[33] Yamazaki E, Murayama M, Nishikawa N, Hashimoto N, Shoyama M, Kurita O. Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells. Solar Energy 2007;81:512–6.
[34] Polo AS, Iha NYM. Blue sensitizers for solar cells: natural dyes from Calafate and Jaboticaba. Solar Energy Materials and Solar Cells 2006;90:1936–44.
[35] Calogero G, Marco GD. Red Sicilian orange and purple eggplant fruits as natural sensitizers for dye-sensitized solar cells. Solar Energy Materials and Solar Cells 2008;92:1341–6.
[36] Ali RAM, Nayan N. Fabrication and analysis of dye-sensitized solar cell using natural dye extracted from dragon fruit. International Journal of Integrated Engineering 2010;2:55–62.
[37] Bazargan MH. Performance of nanostructured dye-sensitized solar cell utilizing natural sensitizer operated with platinum and carbon coated counter electrodes digest. Journal of Nanomaterials and Biostructures 2009;4:723–7.
[38] Calogero G, Marco GD, Cazzanti S, Caramori S, Argazzi R, Carlo AD, et al. Efficient dye-sensitized solar cells using red turnip and purple wild Sicilian prickly pear fruits. International Journal of Molecular Sciences 2010;11:254–67.
[39] Kumara GRA, Kaneko S, Okuya M, Onwona-Ageyeman B, Konno A, Tennakone K. Shiso leaf pigments for dye-sensitized solid-state solar cell. Solar Energy Materials and Solar Cells 2006;90:1220–6.
[40] Zhou H, Wu L, Gao Y, Ma T. Dye-sensitized solar cells using 20 natural dyes as sensitizers. Journal of Photochemistry and Photobiology A: Chemistry 2011;219:188–94.
[41] Hernández-Martínez AR, Vargas S, Estevez M, Rodríguez R. Dye-sensitized solar cells from extracted bracts bougainvillea betalain pigments. In: 1st International Congress on Instrumentation and Applied Sciences. 2010. p. 1–15.
[42] Chang H, Wu HM, Chen TL, Huang KD, Jwo CS, Lo YJ. Dye-sensitized solar cell using natural dyes extracted from spinach and ipomoea. Journal of Alloys and Compounds 2010;495:606–10.
[43] Lai WH, Sub YH, Teoh LG, Hona MH. Commercial and natural dyes as photosensitizers for a water-based dye-sensitized solar cell loaded with gold nanoparticles. Journal of Photochemistry and Photobiology A: Chemistry 2008;195:307–13.